

## THE SHIELDING OF EXTERNAL ELECTRIC FIELDS IN ATOMS REVISITED

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An atom, placed in an external homogeneous electric field, will show a complex charge distribution. The pattern of the polarization density distribution, obtained by subtracting the original electron cloud from the one of the polarized atom, can easily be explained by considering the various orbitals. Poisson's equation relates the induced field to the polarization density distribution.

Recently Dzuba et al. [1] analyzed the response of an atomic system to an external static homogeneous electric field  $E_{\text{ex}}$ . They calculated  $E_{\text{pol}}(\mathbf{r})$ , the field produced by the polarized electron cloud as a function of position and found unexpected oscillatory behaviour [2].

Robinson [3] reacted to this paper and was able to explain the oscillatory behaviour by assuming the atom to have multiply occupied shells which are well separated radially. Our present work on the charge distribution in small molecules suggests an alternative explanation, which does not require the unphysical assumption of radially separated shells and yields understanding without the need to carry out extensive calculations.

When we place a closed shell atom such as Ne in a weak external electric field,  $E_{\text{ex}}$ , the resulting electron density distribution,  $\rho^E(\mathbf{r})$ , shows a complex pattern. To bring out the details, the original electron density distribution,  $\rho^0(\mathbf{r})$ , is subtracted and the difference, the so-called polarization density, is shown in fig. 1. The calculations were carried out with the Hartree-Fock-Slater method, using Slater-type orbitals as basis set. The method is described by Krijn and Feil [4].

The pattern of the polarization density can easily be understood as follows: the total electron density is the sum of the densities of the occupied orbitals:

$$\rho^E(\mathbf{r}) = 2 \sum_i |\phi_i^E(\mathbf{r})|^2, \quad (1)$$

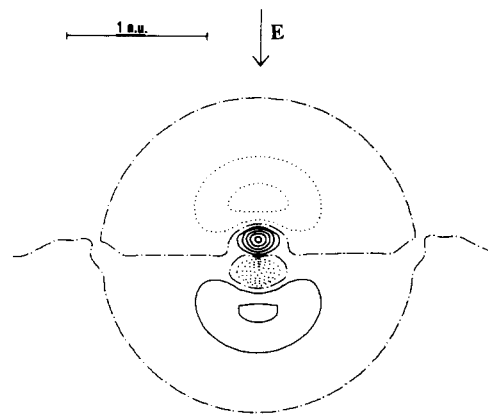


Fig. 1.

in which double occupancy is assumed. The atomic orbitals of the polarized atom differ slightly from the ones in the free atom, and can be obtained by mixing in unoccupied orbitals  $\phi_j^0$  of the proper symmetry:

$$\phi_i^E(\mathbf{r}) = \phi_i^0(\mathbf{r}) + \sum_j c_{ij} \phi_j^0(\mathbf{r}). \quad (2)$$

Mixing in of occupied orbitals does not change the Slater determinant.

Since the effect of the electric field is small, the coefficients  $c_{ij}$  can be calculated by second order perturbation theory:

$$c_{ij} = \frac{E \langle \phi_j^0 | \mathbf{r} | \phi_i^0 \rangle}{\epsilon_i - \epsilon_j}, \quad (3)$$

in which  $\epsilon_i$  and  $\epsilon_j$  are orbital energies.

For qualitative purposes we can restrict the summation to the coupling of the highest occupied atomic orbital with the lowest unoccupied one with the proper symmetry. In case of a field in the  $z$ -direction, the  $2p_z$  orbital of Ne is coupled with the  $3s$  orbital.

The energy difference in the numerator of (3) makes other contributions less significant.

The contribution to the total electron density distribution by the polarized orbital  $2p^{(E)}$  is given by

$$2|2p_z^{(E)}|^2 = 2|2p_z^0|^2 + 4c \times 2p_z^0 \times 3s^0 + \dots \quad (4)$$

Consequently the contribution to the polarization density is

$$\Delta\rho(\mathbf{r}) = 4c \times 2p_z^0(\mathbf{r}) \times 3s^0(\mathbf{r}) . \quad (5)$$

The polarization density of fig. 1 shows the topology of the product of the  $2p$  and the  $3s$  orbitals. Since these orbitals are hydrogenic in character, the product can easily be visualized: the number of nodal points on the  $z$ -axis is the sum of the number of nodes of the individual orbitals, i.e. one for the  $2p$  and four for the  $3s$  orbital, making a total of five, one of which is on the origin.

We now turn to the electric field. Sternheimer [2], in his pioneering work on the electronic polarizabilities of ions, showed that since the nucleus is stationary, the Hellmann–Feynman force extended by the electron cloud must compensate the effect of the external field  $E_{\text{ex}}$ . He calculated the contributions of the different polarized orbitals to the electric field at

the origin and showed the effect of core polarization to be small. This result holds for the outcome of Hartree–Fock–Slater calculations as well. Thus the local field due to the polarization charge is equal in size and oppositely directed to the external field. Outside the atom the fields of the nucleus and the unpolarized electron cloud cancel and we observe the field of the induced dipole moment, directed parallel to the external field  $E_{\text{ex}}$ . To relate the induced electric field inside the atom to the polarization density distribution discussed above we use Poisson's equation. For points on the  $z$ -axis it gives

$$\delta E_z / \delta z = \rho / \epsilon_0 . \quad (6)$$

Subtracting from both sides the quantities belonging to the undisturbed atom we are left with the required relation. The increase and the decrease of the induced electric field thus follows the same pattern as the polarization density distribution, with the maxima and minima of the field coinciding with the nodal points of this distribution.

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